GEOCHEMICAL ANALYSIS OF SELECTED METAL CONCENTRATIONS OF THE "BEREA SHALE"

A Thesis

Presented in Partial Fulfillment of the Requirements
for the Degree Bachelor of Science

by

Todd J. Aebie

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Advisor
Department of Geology
and Mineralogy

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ABSTRACT

This thesis presents geochemical evidence to support the metal concentrations of Ti, Cr, Mn, Fe, Ni, Cu, and Zn found in the "Berea Shale" of the First Berea Formation. The x-ray fluorescence and x-ray diffraction equipment were used to sample the "Berea Shale" for its relative abundances of metals and clays. The data collected from the "Berea Shale" were then compared to similar data from core OH01 of the Ohio Shale, which was used as a standard. This data was then plotted on graphs of concentration versus concentration, and concentration versus depth, to determine the similarities and differences between these two shales.

INTRODUCTION

The objective of this study was to determine concentrations of selected elements in a shale bed of the Berea Sandstone. Black shale forms under reducing conditions and may contain metals by absorption on clays, oxides and hydroxides, organic material, and in sulfide minerals. The metals in this study are Ti, Cr, Mn, Fe, Ni, Cu, and Zn.

The shale samples were collected from a core of Berea Sandstone drilled by Opex, Inc. on October 26, 1981. The well called Lawrence #1, is located in Section 22, Berne Township, Athens County, Ohio. The total depth of the hole was 1674 feet of which 26 feet were cored between depths of 1539-1565 feet in the so-called "First Berea" Formation.

The shale bed is a fine-grained terrigenous rock, (Potter, 1984) which most likely formed in the distal portion of the Bedford delta which developed during the Mississippian Period in northern and central Ohio. The shale bed formed at the margin of a prograding delta under environmental conditions that changed frequently. The environments during shale deposition were reducing and then changed abruptly to oxidizing which was accompanied by deposition of silty sand.

The metal concentrations of the shale in the Berea core were compared to those of a core of the Ohio Shale (OH01). This core was drilled in Huntington Township, Ross County, Ohio and is known as the John Hirsh well No.1. The well was drilled in 1945 for the Ohio State University Engineering Experiment Station. The depth of the well is 561 feet after reaching the Ohio Shale at a depth of 123 feet.

The Ohio Shale was selected as a basis for comparison because it also formed in a reducing environment during the preceding Devonian Period in a foreland basin which received sediments from the east and north. These sediments originated from the Canadian shield and from the early Appalachian Mountains.

ANALYTICAL PROCEDURES

The core was sampled at approximately 15 cm intervals and the shale samples weighed approximately 4-6 grams, which was sufficient to make the 3 grams of powder needed for the analysis by x-ray fluorescence. The samples were numbered from 1 to 13 increasing downward from the top of the core as shown in Table 1. Three grams of powder were compressed into pellets with 6 grams of crystalline boric acid used as a backing.

The powdered shale samples were <u>not</u> leached with dilute acid prior to analysis because such treatment would have dissolved not only carbonates but also other minerals, including sulfides and oxides of metals. In addition, acid treatment can displace adsorbed metal ions from clay minerals and oxide particles and thereby alter the metal content of the shale samples.

The pellets were analyzed for Ti, Cr, Mn, Fe, Ni, Cu, and Zn. The U.S.G.S. standard AGV-1 was run at intervals as a monitor. Each sample was analyzed in duplicate and the results were averaged in order to enhance their reliability.

The calibration for each of the elements was based on triplicate

TABLE 1: Average Metal Concentrations in the Berea Shale

Sample No.	Depth below top of shale		Ti ppm	Cr ppm	Mn ppm	Fe %	Ni ppm	Cu ppm	Zn ppm
1	0cm	ave.	8171	149	499	6.81	77	45	100
		range	78	18	7	0	1	3	1
2	15.3cm	ave.	7315	150	465	6.75	62	44	100
		range	42	5	26	.02	3	1	2
3	27.4cm	ave.	7001	149	500	6.33	70	42	97
		range	87	5	3	.04	2	4	1
4	43.5cm	ave.	6550	133	502	5.95	73	46	87
		range	314	10	36	.02	2	1	1
5	59.4cm	ave.	7207	152	550	7.45	63	49	105
		range	55	17	12	.03	1	3	2
6	74.0cm	ave.	7136	170	467	6.70	67	42	98
		range	236	12	32	.03	1	0	3
7	91.4cm	ave.	6718	125	482	6.24	61	43	98
		range	224	12	3	.03	5	1	3
8	103.6cm	ave.	6849	152	403	7.30	96	48	106
		range	110	9	1	.01	2	2	1
9	120.8cm	ave.	6757	145	477	5.58	58	39	93
		range	17	4	21	.02	2	3	2
10	136.8cm	ave.	6316	115	432	5.34	54	40	152
		range	15	11	17	.02	2	1	3
11	150.4cm	ave.	7121	164	502	6.75	73	44	103
		range	146	4	7	.01	1	2	1
12	164.0cm	ave.	7276	148	494	5.04	54	40	94
		range	127	3	37	.03	2	0	0
13	179.5cm	ave.	6083	147	574	6.57	62	45	103
		range	1114	20	4	.01	3	3	2

analyses of five U.S.G.S. rock standards (W-1, G-1, AGV-1, BCR-1, GSP-1) and is expressed as linear equations listed in Table 2. The equations are expressed in terms of the x-ray intensity ratios of the K-alpha peaks relative to MoK-alpha-Compton-scattered radiation. The concentrations of the elements were expressed in parts per million by weight (ppm), except Fe which was calibrated as Fe_2O_3 in percent by weight. The individual measurements are compiled in Appendix A and the averaged concentrations are listed in Table 1.

The shale samples were also analyzed by x-ray diffraction to determine their mineral compositions. The clay minerals which were identified are montmarillionite, illite, and kaolinote-chlorite. In addition, quartz is present in all samples. The results from this analysis are listed in Table 3. Table 4 shows the relative concentrations of the minerals based on a semi-quantitative parameter, X, to provide a means of comparing the results.

INTERPRETATION OF THE DATA

A) Mineral Compositions

The results of the x-ray diffraction analysis show that the abundance of the clay minerals in the core are approximately uniform throughout the core. There is little change in the abundancies of the minerals within the core. Although no major differences in the mineral composition were identified, certain smaller relationships were observed. For example, the last two samples (12 and 13) show the greatest relative abundances of quartz compared to the other samples.

TABLE 2: Calibration equations for metals analyzed in this study based on U.S.G.S. Rock Standards

$$Mn = 16857.337 \frac{Mn}{Mo} + 92.636ppm$$

$$Cr = 27523.911 \frac{Cr}{Mo} + 7.278ppm$$

$$Ti = 51949.22 \frac{Ti}{Mo} + 2242.02\ ppm$$

$$Zn = 2708.159 \frac{Zn}{Mo} - 119.349ppm$$

$$Cu = 2006.153 \frac{Cu}{Mo} - 199.371ppm$$

$$Ni = 6224.170 \frac{Ni}{Mo} - 20.725ppm$$

$$Fe_2O_3 = 1.4522 \frac{Fe}{Mo} + 0.735\%$$

Concentrations in AGV-1

Zn = 84.0 ppm	Mn = 763 ppm
Cu = 59.7 ppm	Cr = 12.2 ppm
Ni = 18.5 ppm	Ti = 6190 ppm
Fe = 47,281 ppm	

TABLE 3: X-Ray Diffraction Data of the "Berea Shale"

	Mont.	Illite	Kaol-Chl	Qtz-Ill
		(cts/sec)		
Sample no.				
1	120	475	375	530
2	95	370	360	580
3	80	410	385	580
4	90	530	350	610
5	90	330	350	490
6	115	580	460	480
7	85	435	390	550
8	55	300	285	515
9	80	360	325	560
10	NA	NA	NA	NA
11	NA	NA	NA	NA
12	63	375	250	875
13	75	350	325	750

Na: Results are not reliable due to equipment malfunctions.

TABLE 4: X-Ray Diffraction Data based on the semi-quantitative parameter X

Sample No.	Mont.	Illite	Kaol-Chl	Qtz-Ill
1	4x	4x	4x	3x
2	4x	3x	4x	3x
3	3x	3x	4x	3x
4	4x	4x	4x	3x
5	4x	3x	4x	3x
6	4x	4x	4x	3x
7	3x	4x	4x	3x
8	2x	3x	3x	3x
9	3x	3x	3x	3x
10	Na	Na	Na	Na
11	Na	Na	Na	Na
12	3x	3x	3x	4x
13	3x	3x	3x	4x

Na: Results are not reliable due to equipment malfunction.

X: X is a semi-quantitative parameter which is calculated to more easily help to interpret the results from the X-Ray Data.

B) Geochemical Coherence

The elements were graphed in Figures 1 to 6 against Fe in order to determine to what extent the other metals are associated with Fe in the Berea shale samples. Many of the elements appear to correlate positively with the Fe. The deviant points, plotted as circles, were not used in the least-squares regression of the data sets. The results of the regression in Table 5 include the slope, intercept, and the correlation coefficient for each metal versus Fe.

The results in Table 6 demonstrate that Cu and Zn show the best correlation with Fe, as expected since Cu and Zn are chalcophile elements and therefore should show a good association with the iron sulfides. In addition, Ni is correlated with Fe, but not as well as Cu and Zn even though Ni also forms sulfides with Fe. The correlation coefficients for Cu and Zn are 0.899 and 0.809, respectively, while that of Ni is 0.706. The correlations of Cu, Zn, and Ni with Fe may also be caused by the adsorption of metallic cations on the surfaces of Fe-oxide and hydroxide coatings and particles.

The intercepts of the linear equations linking the chalcophile elements to Fe are small and their slopes are positive. The small intercept values indicate that Cu and Zn are more strongly associated with Fe perhaps because they occur in the same minerals. For example, it is possible that Cu and Fe entered the shale together in grains of chalcopyrite ($CuFeS_2$), whereas the Zn occurs with Fe in sphalerite (Zn,Fe)S. The Ni-Fe correlation line actually has the lowest intercept

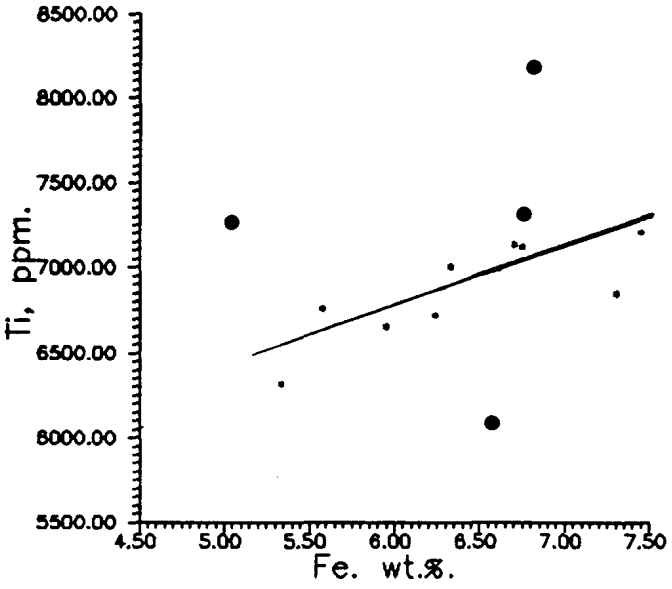

Figure 1

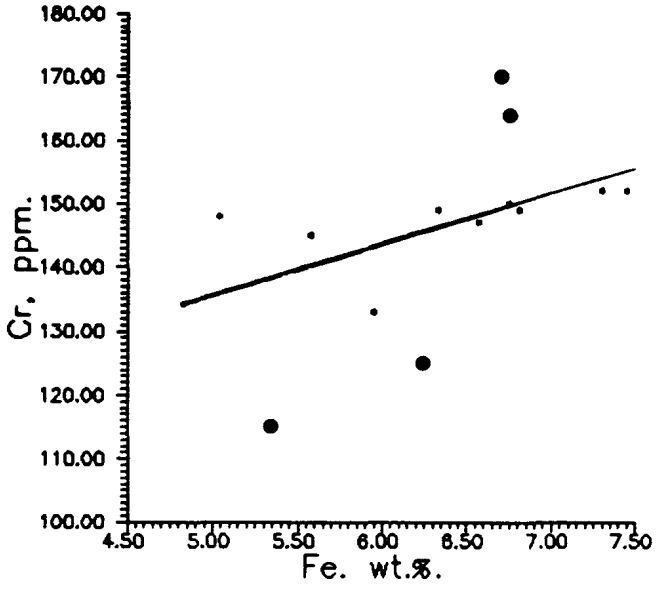

Figure 2

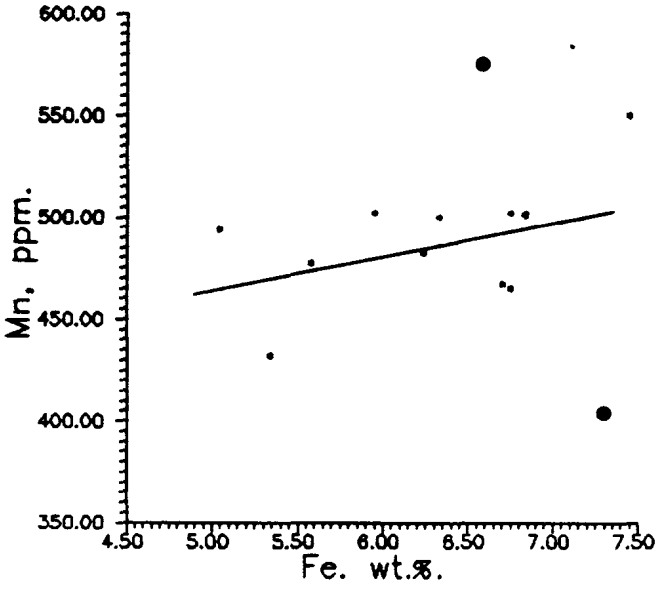

Figure 3

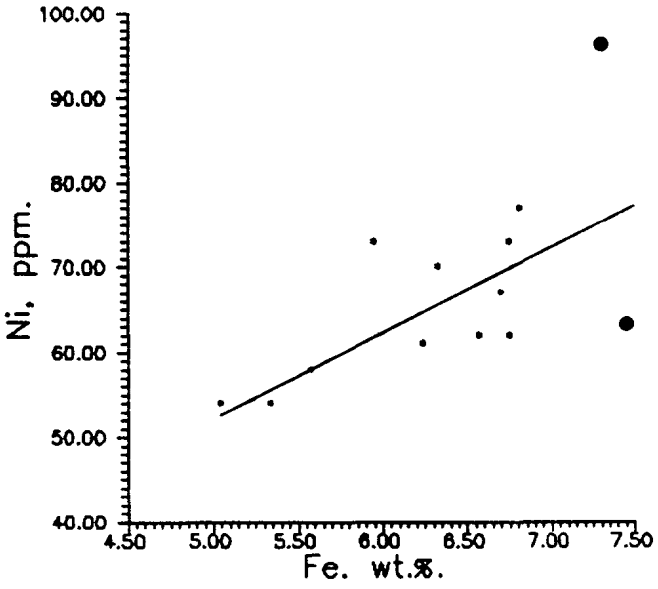

Figure 4

Figures 1-4; Metal Concentrations plotted against Iron

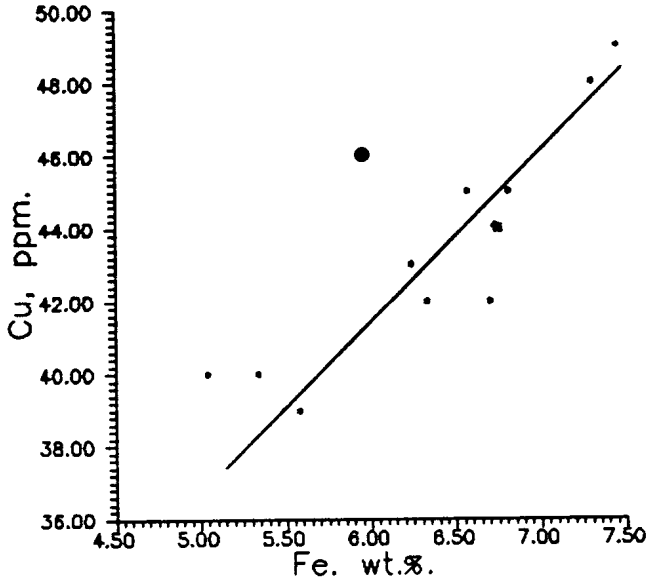

Figure 5

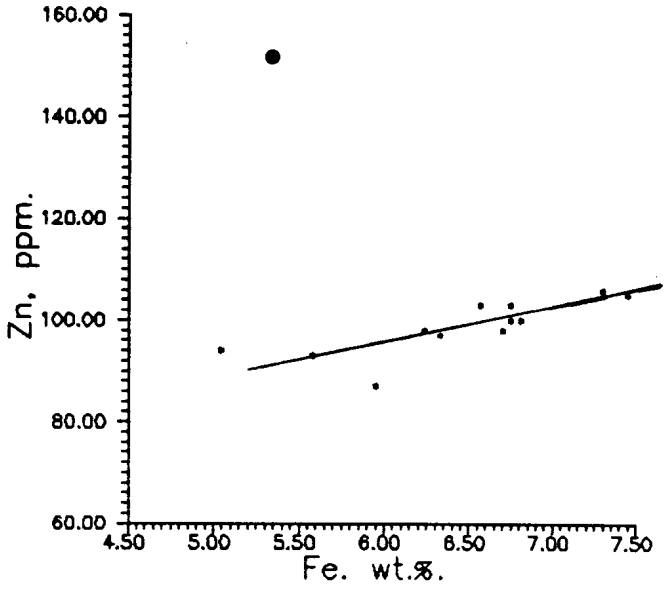

Figure 6

Figures 5-6; Metal Concentrations plotted against Iron

TABLE 5: Least-squares regression of concentration of elements versus Fe

M = slope,
B = intercept,
Y = MX + B,

	Corr.	M	B
Ni - Fe	0.706	8.81	9.82
Cu - Fe	0.899	3.82	18.9
Zn - Fe	0.809	6.55	56.3
Mn - Fe	0.686	33.7	272
Cr - Fe	0.637	10.7	77.7
Ti - Fe	0.363	135	6056

TABLE 6: Table of Correlation Coefficients

	Ti	Cr	Mn	Fe	Ni	Cu	Zn
Ti	1.00	0.465	0.335	0.363	0.243	0.088	0.329
Cr	0.465	1.00	0.178	0.637	0.345	0.208	0.055
Mn	0.034	0.178	1.00	0.686	0.324	0.173	0.360
Fe	0.363	0.637	0.686	1.00	0.706	0.899	0.809
Ni	0.243	0.345	0.324	0.706	1.00	0.525	0.194
Cu	0.088	0.208	0.173	0.899	0.525	1.00	0.084
Zn	0.329	0.055	0.360	0.809	0.084	0.194	1.06

(Ni=10 ppm). Evidently Ni is associated with the Fe in these shale samples, but it does not correlate nearly as well as do Cu and Zn. The Ni may be brought into the shale by different sulfide minerals including pentlandite [$(Fe,Ni)_9S_8$], and pyrrhotite [$(Fe,Ni)_{1-x}S$]. However, the Ni ion may also substitute for Fe^{2+} or Mg^{2+} in silicate minerals such as pyroxenes, amphiboles, biotite, and smectite.

The linear correlation coefficients of the other elements (Mn, Cr, and Ti) with Fe are 0.686, 0.637, and 0.363, respectively, and are not as large as those of Zn, Cu, and Ni. The correlation between Ti and Fe is the worst observed, because the correlation coefficient is small (0.363) and the intercept is large. The large intercept means that Ti is only partly associated with Fe, perhaps because Ti has entered the shale as rutile (TiO_2). If that conclusion is valid, the amount of rutile in the shale can be calculated from the intercept of Ti which is equal to 6056 ppm. The corresponding concentration of rutile is 1% by weight, which is small and probably would not be detectable by the use of the x-ray fluorescence.

Chromium (Cr) also correlates poorly with Fe and may have entered the sample in the grains of several minerals including chromite ($FeCr_2O_4$) or in Cr-bearing pyroxenes and/or garnets. The intercept of the Cr line is at 77.7 ppm which implies a probable (Cr_2O_3) concentration of only 0.1% in the shales which is not associated with Fe.

Manganese (Mn) also correlates poorly with Fe indicating that it too was probably brought into the shale by a variety of minerals. Since the Mn^{2+} ion can readily substitute for the Fe^{2+} and Mg^{2+} ions, a large

number of minerals such as amphiboles, pyroxenes, and biotite may be responsible for carrying the Mn into the shale. The intercept of the Mn line is 272 ppm thus indicating that Fe-free MnO_2 is present in the samples at a concentration of approximately 0.04%. The predicted abundances of both Fe-free Cr and Mn minerals is small and is probably undetectable by x-ray diffraction. The intercept values are expressed as a percentage of the average concentrations in Table 7.

COMPARISON TO THE OHIO SHALE CORE OH01

The shale samples from the Berea Sandstone were compared to the Ohio Shale in core OH01. The comparison shows that the shale in the Berea Sandstone is a fairly typical shale, characterized by it's similar mineral compositions. The data for the comparison are listed in Table 8.

From Table 8 it can be stated that the concentrations of Ti, Cr, Mn, and Fe in the "Berea Shale" are greater than those in the Ohio Shale by more than 30 ppm in some cases. The standard deviations of the average concentrations of these elements in the formations do not overlap, indicating that differences in the concentrations are probably real. However, the concentrations of Ni, Cu, and Zn, are lower than those of the Ohio Shale. These errors in the concentrations do overlap, except for that of Ni.

The percent errors of all elements in the "Berea Shale" are smaller than the corresponding errors in the Ohio Shale. Therefore, the "Berea Shale" is more uniform in composition than the Ohio Shale in the

TABLE 7: Intercept expressed as percentage of average concentration

Ni = 14.6 %

Cu = 43.0 %

Zn = 54.6 %

Mn = 55.7 %

Cr = 53.2 %

Ti = 86.8 %

TABLE 8: Comparison between the "Berea Shale" and the Ohio Shale

	"Berea Shale" (13 Samples)	Well OH01 "Ohio Shale" (37 Samples)
Ti, ppm.	6969 ± 197 (2.8%)	4786 ± 336 (7.0%)
Cr, ppm.	146 ± 10 (6.8%)	91 ± 13 (14%)
Mn, ppm.	488 ± 16 (3.2%)	284 ± 150 (52%)
Fe, %.	6.37 ± .02 (0.3%)	4.05 ± .84 (41%)
Ni, ppm.	67 ± 2 (3.1%)	132 ± 54 (41%)
Cu, ppm.	44 ± 2 (4.2%)	62 ± 23 (37%)
Zn, ppm.	103 ± 2 (1.6%)	148 ± 123 (84%)

OH01 core. The differences in composition could be caused by the fact that core OH01 represents a greater thickness of shale than do the samples from the "Berea Shale".

STRATIGRAPHIC PROFILES

The average metal concentrations in the "Berea Shale" were plotted versus depth to relate the anomalous concentrations of the metals to the stratigraphic positions of the samples. The stratigraphic plots in figures 7 to 13, previously identified anomalous values are shown as circles. These samples can now be re-evaluated to determine whether they are truly anomalous in the sense defined above.

The plots show that the concentrations of all metals generally increase up-section. A regression line was fitted to the data points in each graph to establish the stratigraphic trend and to identify the anomalous values which deviate from that trend. The figures show that some of the values previously identified as anomalous do not actually deviate from the stratigraphic pattern. Moreover, some values which were not considered to be anomalous in the X-Y plots are found to be anomalous in a stratigraphic context.

Based on the stratigraphic profiles, the concentrations of all the elements in each of the samples are classified as either being "anomalous high" (AH), "anomalous low" (AL), or "normal" (N). These determinations are listed in the resulting classification matrix in Table 9 which identifies certain stratigraphic intervals in the core in which one, or several elements have either high or low anomalous

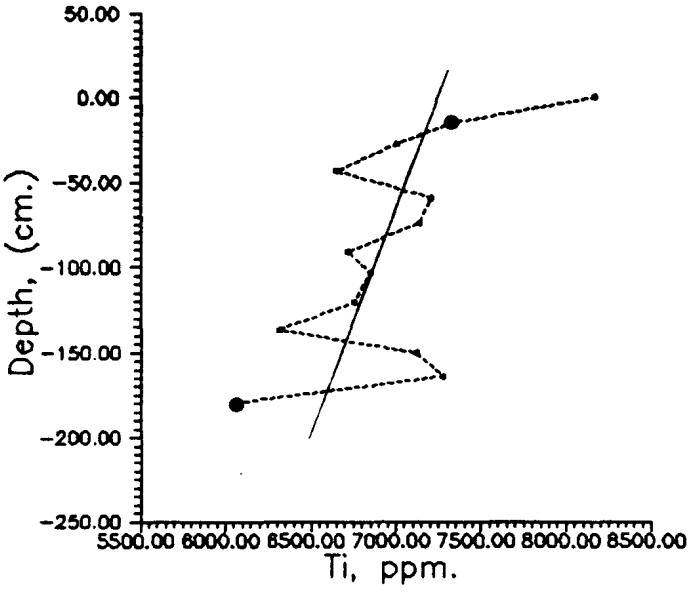

Figure 7

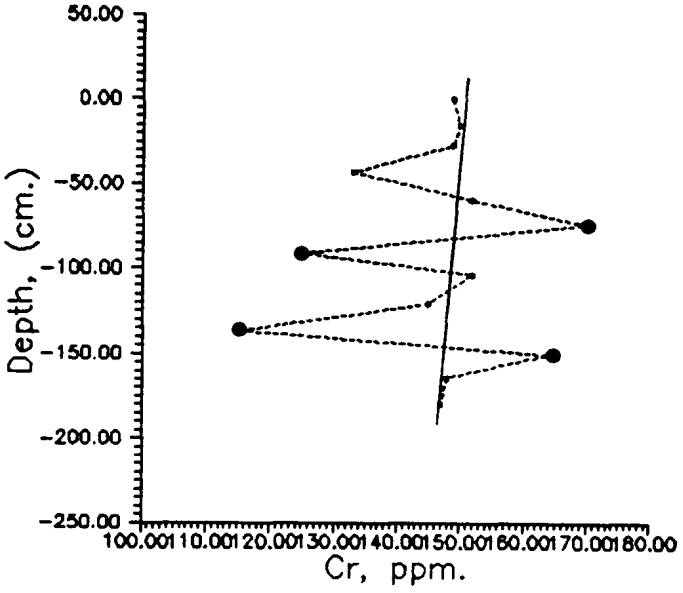

Figure 8

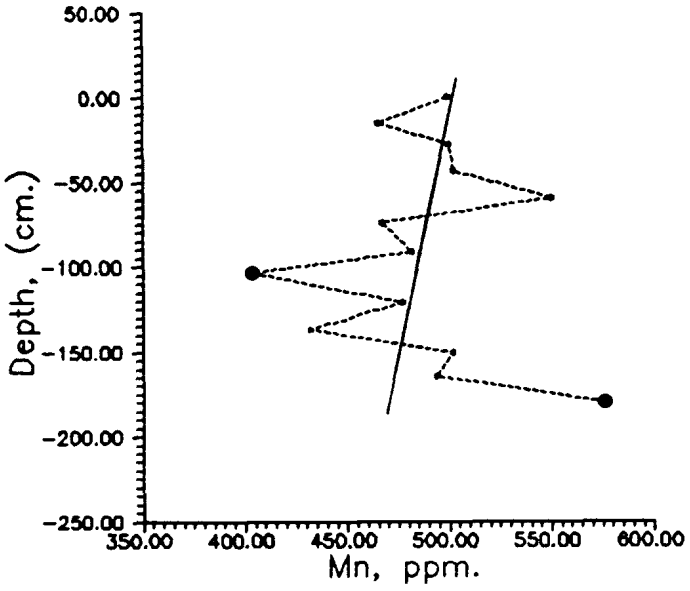

Figure 9

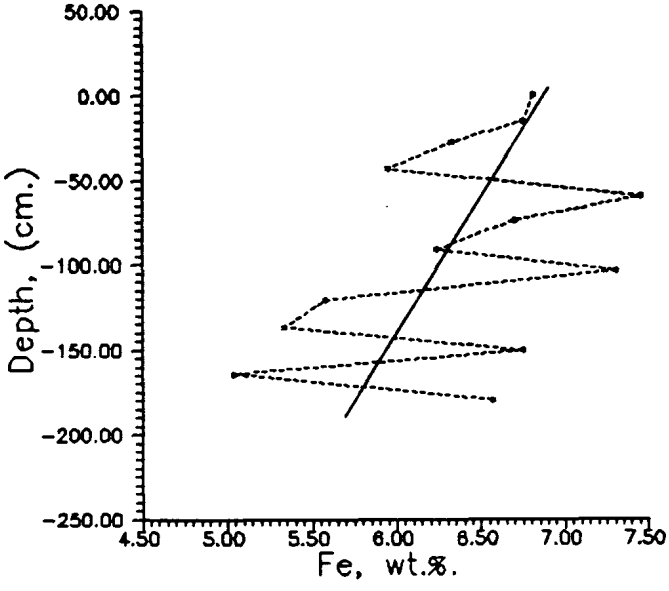

Figure 10

Figures 7-10; Metal concentrations plotted versus Depth (cm).

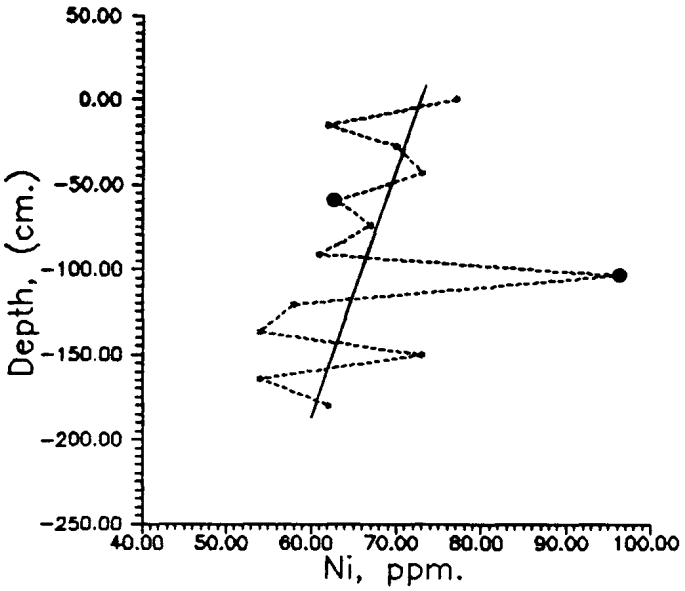

Figure 11

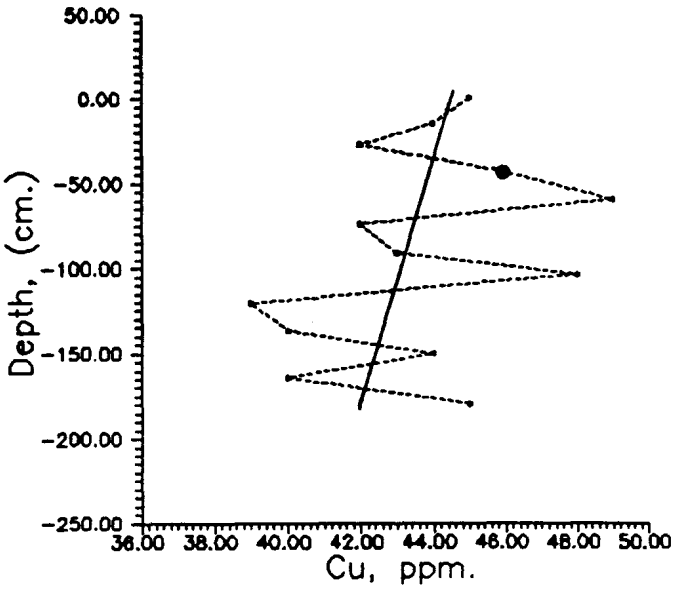

Figure 12

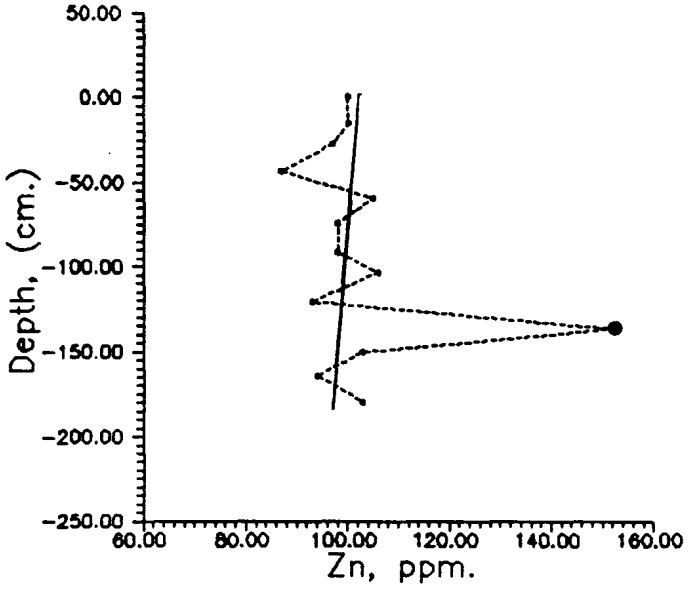

Figure 13

Figures 11-13; Metal concentrations plotted versus Depth (cm).

TABLE 9: Classification Matrix

Depth	Ti	Cr	Mn	Fe	Ni	Cu	Zn
0.0cm	AH	N	N	N	N	N	N
15.3cm	N	N	N	N	N	N	N
27.4cm	N	N	N	N	N	N	N
43.5cm	AL	N	N	AL	N	N	N
59.4cm	N	N	AH	AH	N	AH	N
74.0cm	N	N	N	N	N	N	N
91.4cm	N	AL	N	N	N	N	N
103.6cm	N	N	AL	AH	AH	AH	N
120.8cm	N	N	N	AL	N	AL	N
136.8cm	AL	AL	AL	AL	AL	AL	AH
150.4cm	AH	N	N	AH	AH	N	N
164.0cm	AH	N	N	AL	N	N	N
179.5cm	AL	N	AH	AH	N	N	N

AH = Anomalous High
AL = Anomalous Low
N = Not Anomalous

concentrations. For example, the plot of Cr versus depth, (Figure 8), reveals that the Cr exhibits only two anomalous values instead of four values identified in the X-Y plot. Both of these anomalous concentrations are lower than the average. One of the samples at a depth of 91.4 cm is found to be anomalous with respect to Cr, whereas Fe is normal. This shows that Cr rather than Fe is anomalous at this stratigraphic depth which was not apparent in the Cr-Fe correlation diagram.

From this classification matrix we can observe trends more easily and anomalous results are more quickly noted. For example, the interval from 150.4 cm to 164.0 cm is enriched in Ti, whereas the shale at 136.8 cm and at 179.5 cm is depleted with respect to Ti. Similarly, from 120.8 cm to 136.8 cm Cu is depleted whereas the shale at a depth of 103.6 cm has an anomalously high Cu concentration.

Not only vertical stratigraphic metal anomalies but variations in the metal content in specific horizons are easily observed in Table 8. For example, at the depth of 103.6 cm, Mn is anomalously low in concentration whereas Fe, Ni, and Cu are all enriched. A very interesting layer occurs at the stratigraphic depth of 136.8 cm. Here, all but one of the elements are anomalously depleted except for Zn which is found to be anomalously high. This layer is the only one in which the concentrations of Zn is anomalously high. The enrichment of the Zn and the depletion of this layer in the other metals may be caused by the occurrence of $CaCO_3$ which was detected by the acid test.

CONCLUSION

The later part of the Devonian Period in central Ohio is characterized by the end of black shale deposition and the beginning of sandstone deposition in the First Berea Formation. Selected metals of the "Berea Shale" were analyzed for their concentrations and compared to known values for the same metals in the Ohio Shale. This comparison indicated the metals of the "Berea Shale" were similar in concentration to those of the Ohio Shale, even though the "Berea Shale" was formed during a period of changing depositional environment.

Appendix A; Analyses of powdered shale samples, Lawrence #1 well, Berea Sandstone (upper), Athens Co., Ohio

Sample No.	Depth below top of shale		Ti ppm	Cr ppm	Mn ppm	Fe %	Ni ppm	Cu ppm	Zn ppm
1	0cm		8093	131	492	6.82	78	47	99
			8249	167	506	6.81	76	42	101
		ave.	8171	149	499	6.81	77	45	100
		range	78	18	7	0	1	3	1
2	15.3cm		7272	155	492	6.73	59	43	98
			7375	145	439	6.77	64	45	102
		ave.	7315	150	465	6.75	62	44	100
		range	42	5	26	.02	3	1	2
3	27.4cm		6914	143	503	6.37	68	38	97
			7088	154	497	6.29	71	45	88
		ave.	7001	149	500	6.33	70	42	97
		range	87	5	3	.04	2	4	1
4	43.5cm		6336	143	465	5.97	74	46	85
			6964	123	538	5.94	71	45	88
		ave.	6550	133	502	5.95	73	46	87
		range	314	10	36	.02	2	1	1
5	59.4cm		7151	135	538	7.48	63	46	107
			7262	168	562	7.41	62	52	102
		ave.	7207	152	550	7.45	63	49	105
		range	55	17	12	.03	1	3	2
6	74.0cm		6899	158	435	6.67	65	42	95
			7372	181	498	6.72	68	42	101
		ave.	7136	170	467	6.70	67	42	98
		range	236	12	32	.03	1	0	3

Sample No.	Depth below top of shale		Ti ppm	Cr ppm	Mn ppm	Fe %	Ni ppm	Cu ppm	Zn ppm
7	91.4cm		6942	137	485	6.20	56	42	95
			6494	113	479	6.27	66	44	101
		ave.	6718	125	482	6.24	61	43	98
		range	224	12	3	.03	5	1	3
8	103.6cm		6739	160	404	7.30	94	47	106
			6958	143	402	7.31	98	50	107
		ave.	6849	152	403	7.30	96	48	106
		range	110	9	1	.01	2	2	1
9	120.8cm		6740	141	498	5.57	60	36	91
			6773	148	456	5.60	55	42	95
		ave.	6757	145	477	5.58	58	39	93
		range	17	4	21	.02	2	3	2
10	136.8cm		6330	125	415	5.36	56	40	155
			6301	104	449	5.32	52	41	149
		ave.	6316	115	432	5.34	54	40	152
		range	15	11	17	.02	2	1	3
11	150.4cm		6974	168	509	6.76	72	42	102
			7267	160	495	6.74	73	46	103
		ave.	7121	164	502	6.75	73	44	103
		range	146	4	7	.01	1	2	1
12	164.0cm		7149	145	531	5.01	52	39	94
			7402	150	457	5.06	56	40	94
		ave.	7276	148	494	5.04	54	40	94
		range	127	3	37	.03	2	0	0
13	179.5cm		4969	167	578	6.56	65	42	101
			7197	127	570	6.58	59	48	105
		ave.	6083	147	574	6.57	62	45	103
		range	1114	20	4	.01	3	3	2

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